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Published in:
Physical Review Letters

DOI:
10.1103/PhysRevLett.77.3339

Velocity and Charge State Dependences of Molecular Dissociation Induced by Slow Multicharged Ions

H. O. Folkerts, R. Hoekstra, and R. Morgenstern

K.V.I. Atomic Physics, RijksUniversiteit Groningen, Zernikelaan 25, 9747 AA Groningen, The Netherlands

(Received 8 July 1996)

Dissociation of CO molecules by collisions with He^{2+} and O^{7+} at keV energies has been investigated by measuring the charge states and kinetic energies of the ionized fragments in coincidence with each other. As opposed to earlier investigations with fast (MeV) projectiles we find that the kinetic energies of the fragment ions are strongly influenced by the projectiles' charge and velocity; e.g., O^{7+} impact results in *50% less* kinetic energy release in the C^+-O^+ fragmentation than He^{2+} impact. For a qualitative understanding of these effects we invoke the classical overbarrier model. [S0031-9007(96)01442-1]

PACS numbers: 34.50.Gb, 34.70.+e, 82.30.Fi

Fragmentation of molecules induced by primary ionization processes has been studied in recent years by various methods [1]. Besides electrons as ionizing projectiles, also synchroton radiation [2,3], short laser pulses [4], fast ions [5–8], and, recently, also slow multicharged ions [9–12] have been used to remove electrons from the molecules and thus induce bond breaking. The degree of ionization, the electronic state, and the kinetic energy of the resulting fragments generally depend on the primary process, i.e., the ionization of the molecule. By selecting the appropriate method with suitable initial conditions, one might be able to induce fragmentation in a controlled way. Recently, also, new theoretical investigations have been performed [13] in which potential curves of triply ionized CO molecules have been calculated in order to provide insight for the fragmentation patterns of such ions.

The large amount of research effort dedicated to ionization and dissociation of molecules is motivated as well by the processes in their own right as by their significance in mass spectrometry and studies of astrophysical plasmas. For example, in interstellar clouds or planetary atmospheres, dissociative ionization plays an important role not only in the ionization but also in the kinetic energy balance. Because of their large cross sections for electron capture multicharged ions are effective sources of dissociative ionization. We have used such slow multicharged ions as projectiles to induce fragmentation of CO molecules. In this case, one expects that during the collision, i.e., in a time interval that is short as compared to typical molecular vibration times, several weakly bound electrons can simultaneously be transferred from the CO molecule to the multicharged. This mechanism is different from ionization by electron impact or synchrotron radiation, where mostly only one strongly bound electron is removed in the primary process, or from ionization with short laser pulses, where the interaction with the radiation is over a time range comparable with, or even much longer than, typical vibration times.

Since electron transfer to multiply charged projectiles can take place at internuclear distances that are large as compared to molecular dimensions, one expects a "gentle" ionization, leading to a relatively low kinetic energy of the resulting fragments. During recent years, several studies of molecular fragmentation by multiply charged ions have been performed [8–12]. In the only investigation [8] where the projectile charge was systematically varied, no major influence of this charge on the kinetic energy release to the fragments was observed. As opposed to that work, we now use significantly lower kinetic projectile energies (keV instead of MeV). Our experimental results presented in this paper clearly show a pronounced influence of the projectile's charge and velocity on the energy distribution of the resulting fragments.

The ionization and dissociation can be described as a two-step process:

$$A^{q+} + \mathrm{CO} \rightarrow A^{(q-r+s)+} + \mathrm{CO}^{(r)+*} + se^- \qquad (1)$$

and

$$\mathrm{CO}^{r+} \rightarrow \mathrm{C}^{t+} + \mathrm{O}^{(r-t)+} + U_{\mathrm{KER}}\,, \qquad (2)$$

where U_{KER} is the kinetic energy released in the dissociation.

In the experiments a continuous beam of $^3He^{2+}$ or O^{7+} ions is extracted at 3 to 16 kV from the ECR ion source installed at the atomic physics facility, KVI Groningen. The collimated ion beam with a diameter of 1 mm is crossed with a gaseous CO molecular target with a full width at half maximum of 3 mm. The target pressure was about 0.4 mPa and the beam intensity was adjusted to $\sim$100 pA. The resulting molecular ions and charged molecular fragments are extracted perpendicularly to the ion beam and via a specially designed electrostatic lens system injected into a reflectron mass spectrometer [14]. The design of the extraction and transport system is such that the high resolution of the mass spectrometer can be exploited. Details will be presented in a forthcoming paper by Folkerts *et al.* [15].

With a time-to-amplitude converter (TAC) we have measured time-difference spectra by starting the TAC on the first arriving fragment and using the signal from the

second charged fragment as a stop. With this coincidence technique only $C^{q+} + O^{r+}$ ion pairs are detected.

To determine the kinetic energy of the fragments we have exploited the fact that at low extraction field most of the energetic fragments will be intercepted by the entrance diaphragm of the spectrometer. Only particles ejected within a small angle with respect to the detection axis can be detected. In singles time-of-flight spectra this gives rise to a double peak structure. Ions with their initial velocity towards the spectrometer (forward emitted fragments) have a shorter flight time than the ones with the initial velocity in the opposite direction (backward emitted fragments) since the latter ones first have to be turned around in the electric field before they can reach the spectrometer aperture. In the coincidence measurements, for every measured $C^{q+} + O^{r+}$ ion pair, one of the fragments is emitted in the forward direction and one in the backward direction. Therefore, there are two combinations leading to two peaks in the time spectrum which are separated by a time interval (ΔT) which is equal to the sum of the time differences between the forward and backward emitted C^{q+} fragments and between the forward and backward emitted O^{r+} fragments.

In Fig. 1 the time-difference spectrum for collisions with 2 keV/amu He^{2+} ions is shown. In the spectrum the first peak (about 2 μs) corresponds to the situation where the time measurements have been started by a backward emitted C^+ and stopped by a forward O^+, while the second peak is due to a start from a forward C^+ and a stop from the corresponding backward O^+. Two peaks associated with the $C^{2+} + O^+$ combinations are found at 6 μs and 6.5 μs. The position of the $O^{2+} + C^+$ contribution is marked, but the signal is too low to be separated from the background of accidental coincidences.

For the dissociation of a diatomic molecule the relation between ΔT and the kinetic energy release (U_{KER}) is given by

$$\Delta T = \frac{q + r}{qrE}\sqrt{8\mu U_{\mathrm{KER}}}, \qquad (3)$$

where q and r are the charge states of the fragments, E is the extraction field, and $\mu = m_1 m_2/(m_1 + m_2)$ with m_1, m_2 the masses of the fragments.

We have used this relation to transform the time-difference spectra into kinetic energy distributions. Doing so, we assume that an ion pair with a well defined initial kinetic energy contributes to a narrow time interval in the time-difference spectrum. Under the experimental conditions, this assumption holds since the fragments are only detected when they are emitted within a small angle with respect to the detection axis [15]. The transmission of the fragments depends on the initial kinetic energy. We have therefore corrected our coincidence data by multiplication with $1/k$, where k is the detection efficiency of the fragment with the lowest transmission.

In Fig. 2 the kinetic energy distributions for the $C^+ + O^+$ ion pair formation are shown for 2, 4, and 11 keV/amu He^{2+} on CO collisions (first column) and for 4 keV/amu O^{7+} on CO (second column). It is clearly seen that the kinetic energy distribution strongly depends on the primary collision process. In Figs. 2(a)–2(c) we see that the average kinetic energy released in the dissociation decreases with increasing collision energy. This strong impact energy dependence over such a small energy range is quite remarkable.

Another striking observation is the difference in the kinetic energy distributions for $C^+ + O^+$ formation induced by O^{7+} and He^{2+} on CO at the same collision energy. The main contribution to the kinetic energy distribution of the $C^+ + O^+$ fragments produced in O^{7+} on CO collisions is found at 6 eV, whereas for He^{2+} collisions the main component lies around 17 eV. From these results we conclude that, in He^{2+} collisions, higher excited states of the transient CO^{2+} molecular ion are populated than in O^{7+} collisions. To understand the experimental results we will discuss the charge exchange processes in the picture of the overbarrier model [16]. We propose that, in spite of the

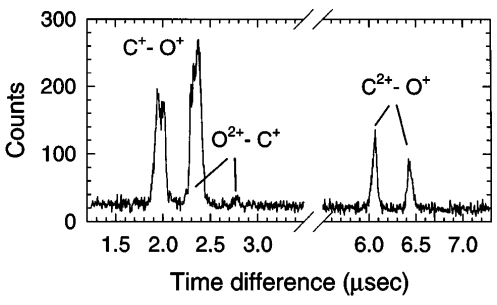

FIG. 1. Time-difference spectrum of ion pairs produced in 2 keV/amu He^{2+} on CO collisions.

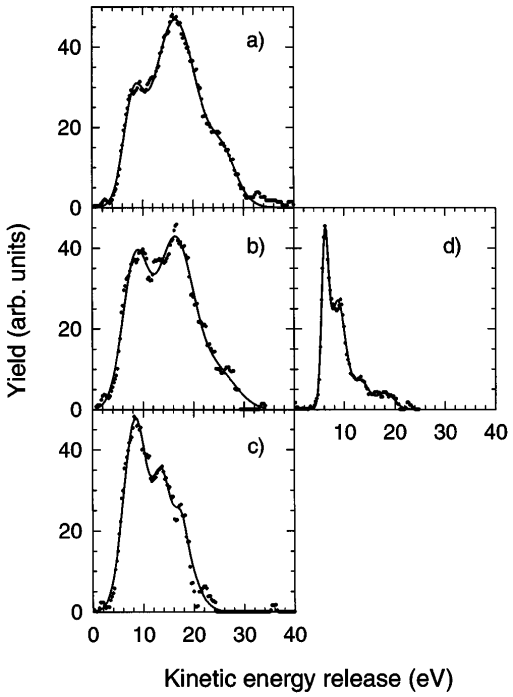

FIG. 2. Kinetic energy distributions for $C^+ + O^+$ ion pair formation for (a) 2 keV/amu He^{2+}, (b) 4 keV/amu He^{2+}, (c) 11 keV/amu He^{2+}, and (d) 4 keV/amu O^{7+} on CO collisions.

molecular nature of CO, the overbarrier model, which has been developed for ion-atom collisions, can be used for a description of electron transfer to highly charged ions, because the collision time is short compared to the vibration time of the nuclei in the molecule, and because capture of the outer electrons takes place at large internuclear distances compared to the size of the molecule. In the model it is assumed that, on the way in of the collision, the electrons of the target become subsequently quasimolecular. On the way out of the collision, the electrons are redistributed over the target and projectile.

In the following we assume that maximally three electrons are active in the collisions, i.e., become quasimolecular. For the ionization potentials of the outer three CO electrons, needed for the overbarrier calculations, we took 13.7, 27.3, and 40 eV, respectively. These values are deduced from the thresholds for CO^{3+} and CO^{2+} transient ion production as observed by Lablanquie *et al.* [2] by means of photoionization, together with the ionization potential for single ionization which has been extracted from potential energy curve calculations [17] under the assumption that the internuclear distance between the C and the O remains fixed during the collision.

With the overbarrier model, we have calculated the binding energies of the captured electrons in the projectile and the recaptured electron in the target. If, on the way out, two electrons are captured by the projectile ion while one is recaptured by the target, this will lead to a CO^{2+} molecular ion which sooner or later will dissociate. The population of excited states is related to the binding energy of the recaptured electron. The kinetic energy of the fragments depends firstly on the excited states of the transient CO^{2+} ion which are populated in the charge exchange process, and secondly on the final dissociation limit.

The results of the calculations for the total binding energy of the two outer CO electrons after capture by He^{2+} and O^{7+} are shown in Figs. 3(a) and 3(b), respectively. The width of the reaction windows are calculated as proposed by Hoekstra *et al.* [18] for a collision energy of 4 keV/amu.

In Fig. 3(a) the reaction window is drawn for the capture of the two outer CO electrons. The summed binding energy of the two outer electrons in CO is 41 eV. According to the overbarrier model, the binding energy after capture will be the same since in both cases the electrons are bound in the Coulomb field of a doubly charged nucleus. To compare the so-found binding energy with the energies of the real $He(nl, n'l')$ states, these states are also indicated in the figure. From Fig. 3(a) it is seen that the reaction window lies in between the $He(1s, 2l)$ and the $He(2l, 2l')$ states. This position indicates that the capture of the outer two electrons is unlikely.

According to the model, capture of more strongly bound CO electrons is preferred. The reaction window for the capture of the second and third electron overlaps exactly with the $He(1s, 2l)$ states. This hints at a strong population of excited CO^{2+} states with about 20 eV excitation energy, because the outer electron is recaptured with a binding energy of 21 eV (FWHM = 8 eV). The kinetic energy released by (pre)dissociation to the third, fourth, or fifth dissociation limit will be between 16 and 19 eV. This can explain the main contribution around 17 eV in the experimentally found kinetic energy distribution.

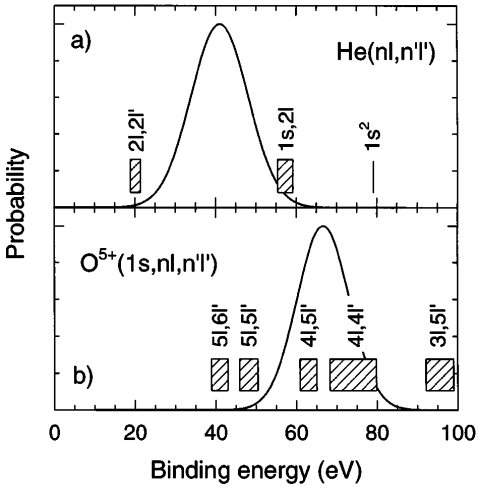

FIG. 3. Reaction windows for two-electron capture in collisions of 4 keV/amu He^{2+} (a) and O^{7+} (b) on CO, as calculated from the classical overbarrier model for the situation in which the two outer CO electrons are captured.

However, the decrease of the kinetic energy release with increasing collision energy is difficult to understand within the overbarrier model. In view of the fact that the collision time (in the order of 0.2 fs) is short as compared to molecular vibration times (20 fs) and that typical impact parameters at which electron transfer takes place (0.3–0.5 nm) are large as compared to the CO equilibrium separation (0.113 nm), it is clear that the kinetic fragment energies are not determined by direct heavy particle interactions but exclusively, in an indirect way, via the electronic configuration. Apparently, the electronic structure of the CO^{2+} molecule produced in the primary collision process is influenced by the amount of time during which the projectile is still in the vicinity of the molecular ion. At low collision energies, electron-electron correlation effects might be responsible for the formation of configurations which lead to a larger kinetic energy release during dissociation.

Electron transfer to O^{7+} is substantially different from capture by He^{2+} because, for O^{7+}, a large number of states can be populated almost resonantly as can be seen in Fig. 3(b). In this figure the reaction window for capture of the two outer CO electrons is shown together with the binding energies of the various $O^{5+}(1s, nl, n'l')$ configurations which are calculated with the Cowan code [19,20]. We see that the reaction window coincides with $O^{5+}(1s, 4l, nl')$ states. Since the capture of the outer two CO electrons results in the population of lower-lying states of CO^{2+}, this supports the experimental

observations of Fig. 2(d), where we see a relatively high yield of low kinetic energy $C^+ + O^+$ fragments.

To conclude, we have studied the dissociation of CO induced by electron transfer to He^{2+} and O^{7+} ions. From coincidence time-difference measurements, we have determined the kinetic energy of the fragments formed in the dissociation process. We have observed that the kinetic energy distributions strongly depend on the collision energy and the projectile charge state.

Our observations are qualitatively understood in the framework of the overbarrier model. The potential energy of the populated excited states in CO^{2+} has been calculated from the binding energies of the recaptured electrons. In this way we were able to explain the main contribution to the observed kinetic energy distribution for $C^+ + O^+$ formation by He^{2+} impact. In charge exchange processes between O^{7+} and CO, two-electron capture is a resonant process which causes the relatively high population of lower-lying excited states in CO. Since quasiresonant electron transfer from molecules is possible in a similar way for all highly charged ions, we believe that the results presented here are not specific for O^{7+} ions, but are more generally valid. We therefore conclude that fragmentation induced by collisions with slow highly charged ions, in general, is a gentle process.

This work is part of the research program of the Stichting Fundamenteel Onderzoek der Materie (FOM) with financial support from the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO).

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